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Bicyclo[3.2.1]octa-3,6-dien-2-yl Cation: A Bishomoantiaromate[†]

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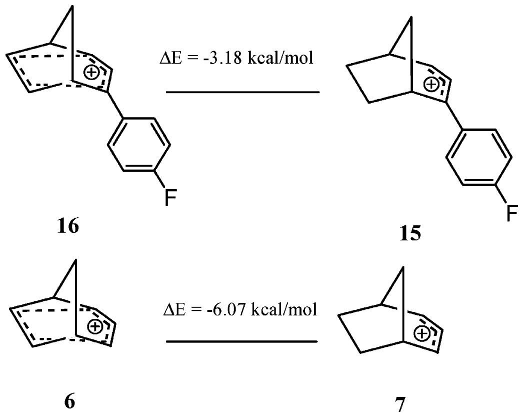

Antiaromatic compounds with a closed loop of 4*n* p-electrons are relatively unstable and often difficult to study. We report in this article the synthesis of alcohols 2-(4'-fluorophenyl)bicyclo[3.2.1]octan-2-ol **11**, 2-(4'-fluorophenyl)bicyclo[3.2.1]oct-3-en-2-ol **12**, and 2-(4'-fluorophenyl)bicyclo[3.2.1]octa-3,6-dien-2-ol **13** and their transformations into corresponding carbocations **14**−**16**, respectively, in a superacidic medium (FSO_3H/SO_2ClF) at −120 °C. Cations **14**−**16** are characterized by NMR analysis (^{1}H, ^{13}C, ^{19}F), and **15** and **16** are further characterized by quenching in $NaOCH_3/H_3COH$ at −120 °C. The relative stabilities of **14**−**16** are determined experimentally by ^{19}F NMR spectroscopy. Cation **16** is found to be experimentally less stable than cation **15** by 3.7 kcal/mol. DFT calculations (structure and energy: B3LYP/6-31G(d); NMR: B3LYP/6-311+G(2d,p)) are performed for alcohols **11**−**13** and bicyclo[3.2.1]octyl cations **6**, **7**, **9**, **14**−**16**, **26**, **28**, and **30**. In the case of **11**−**16**, data from DFT calculations is in good agreement with experimental data. Because 6,7-dimethylenebicyclo[3.2.1]oct-3-en-2-yl cation **26** is more stable than cation **7** by 1.69 kcal/mol, the inductive effect of sp^2-hybridized carbon atoms C6 and C7 in carbocations **6** and **16** cannot be the reason for the destabilization of **6** relative to **7** and **16** relative to **15**. Destabilization of **6** relative to **7** and **16** relative to **15** and the calculated NICS of **6** (+4.17 ppm) and **16** (+3.3 ppm) document that **6** and **16** are bishomoantiaromates.

Introduction

For cyclic conjugated systems with 4*n* p-electrons, which are destabilized by resonance, Breslow has stamped the concept of antiaromates.[1] Cyclopentadienyl cation **1** is a prototype of an antiaromatic carbocation. The failure of the S_N1 solvolysis of cyclopentadienyl iodide in propionic acid in the presence of $AgClO_4$,[2] the derived low pK_{R+} value of −40,[3] and the paramagnetic susceptibility exaltation of $\Lambda = +32.6$,[4] as calculated by means of ab initio methods, express the antiaromatic character of **1**.

The concepts of homoaromaticity and homoantiaromaticity were made popular by Winstein.[5] Cyclic homoconjugated ($4n + 2$) p-electron systems should be stabilized, whereas 4*n*

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[†] Stable carbocations, 35th communication. Volz, H.; Shin, J.-H.; Miess, R. *J. Chem. Soc., Chem. Commun*. **1993**, 543−544.

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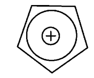
p-electron systems should be destabilized. Although homoaromatic carbocations are already well known, our knowledge of homoantiaromatic carbocations is only scanty.[6] The NMR analysis of cations **2** and **3** have shown that they possess no homoantiaromatic cation character (**2′**). They are considered to be cyclopentenyl-like cations with charge delocalization into the fused-on cyclopropane ring.[7] Solvolysis studies of *p*-nitrobenzoates **4** and **5** in acetone(aq) show that **5** reacts 235 times more slowly than **4**.[8] The authors discuss the bishomoantiaromaticity of intermediary carbocation **6** in the solvolysis of **5** as the reason for the decreased reactivity of **5** relative to that of **4** and not the inductive effect of the olefinic group (C6−C7). Hart and Kuzuya succeeded in observing nonamethylbicyclo-[3.2.1]octa-3,6-dien-2-yl cation **9** at −90 °C in a superacidic solution as a static cation, which at −50 °C rearranges irreversibly into corresponding nonamethylbicyclo[3.3.0]octadienyl cation **10**.[9] As the cause of this rearrangement, the authors also discuss the bishomoantiaromaticity of **9**. Jiao and Schleyer have found, in the context of ab initio calculations on level RMP2 (FU)/6−31 G(d), that because of the exaltations of the magnetic susceptibilities Λ bicyclo[3.2.1]octa-3,6-dien-2-yl anion **8** ($\Lambda = -11.7$) is a bishomoaromate and bicyclo[3.2.1]octa-3,6-dien-2-yl cation **6** ($\Lambda = +8.1$) is a bishomoantiaromate.[10]

If cation **6** is actually a bishomoantiaromate, which is destabilized by the homoconjugation of the (C6−C7) double bond with the allyl cation segment (C2−C3−C4), then it should be less stable than corresponding allyl cation **7**.



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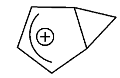

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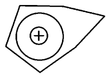

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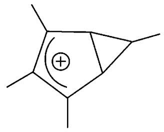

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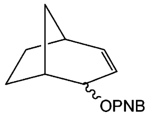

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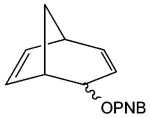

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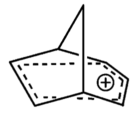

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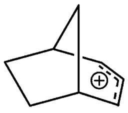

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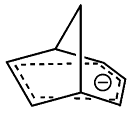

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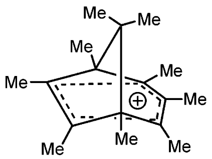

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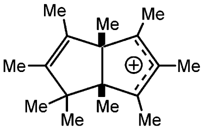

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Computational Methods

For all calculations, we used the density functional program packages provided by the Gaussian 98W suite of programs.[11] The density functional employed is the hybrid functional B3LYP, as implemented in Gaussian 98. To calculate geometries and energies, we used the 6-31G(d) basis set, which includes polarization functions for first- and second-row elements (B3LYP/6-31G(d)). Frequency calculations after each geometry optimization ensured that the calculated structure is a real minimum. The energies were corrected by B3LYP/6-31G(d) zero-point energies. To calculate NMR chemical shifts, we employed the GIAO method, using the 6-311+G(2d,p) basis set, which puts two d-functions on heavy atoms (plus diffuse functions) and one p-function on hydrogens, on the basis of B3LYP/6-31G(d) geometries (B3LYP/6-311+G-(2d,p)//B3LYP/6-31G(d)). The relative stabilities of the carbocations were determined theoretically by isodesmic reactions.[12]

Results and Discussion

Starting out with alcohols 2-(4’-fluorophenyl)bicyclo[3.2.1]-octan-2-ol **11**, 2-(4’-fluorophenyl)bicyclo[3.2.1]oct-3-en-2-ol **12**, and 2-(4’-fluorophenyl)bicyclo[3.2.1]octa-3,6-dien-2-ol **13**, we have prepared in our laboratory carbocations **14**−**16**. The starting materials for the synthesis of the carbinols were the two ketones bicyclo[3.2.1]oct-3-en-2-one and bicyclo[3.2.1]octa-3,6-dien-2-one, which were prepared by known literature methods.[19,20] The reactions of the two ketones with 4-fluorophenyl-magnesium bromide yielded carbinols **12** and **13**. Carbinol **11** was prepared by catalytic hydrogenation of **13**.

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(15) Hydrocarbons **20**, **21**, and **22** with the phenyl substituents in the exo position are in accordance with the DFT calculations (B3LYP/6−31 G(d)) by 2.4 (**20**), 3.8 (**21**), and 3.9 kcal/mol (**22**) and are more stable than the isomeric ones with the phenyl substituent in the endo position.

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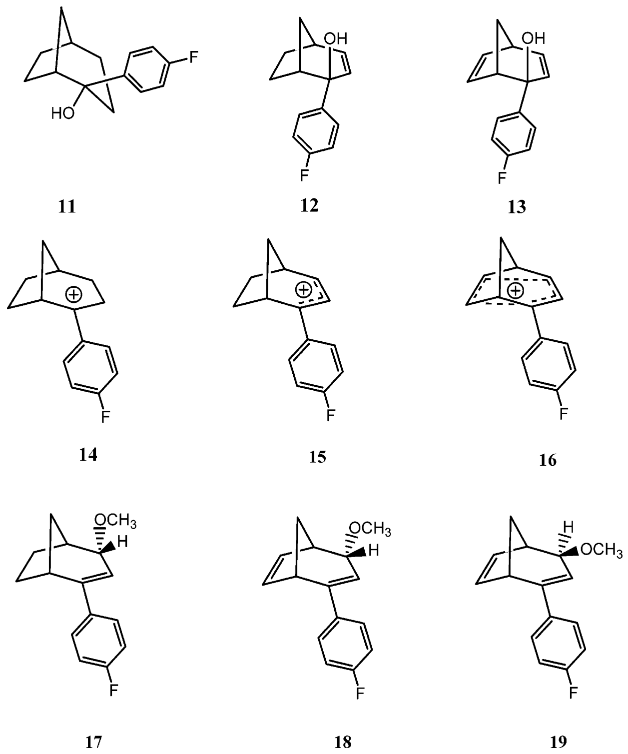
SCHEME 1. 2-(4'-Fluorophenyl)bicyclo[3.2.1]octyl Alcohols 11−13, 2-(4'-Fluorophenyl)bicyclo[3.2.1]octyl Carbocations 14−16, and 2-(4'-Fluorophenyl)bicyclo[3.2.1]octyl Ethers 17−19



Alcohols **11−13** were converted into carbocations **14**, **15**, and expected bishomoantiaromatic cation **16** by dissolving them in a superacid medium (FSO_3H/SO_2ClF) at −120 °C.[13] The ^{1}H, ^{13}C, and ^{19}F NMR spectra of the carbocations were measured in the temperature range of −120 to −50 °C. The chemical proof of cations **15** and **16** was made by their interceptions with sodium methylate/methanol at −120 °C. Carbocation **15** forms methoxyether **17** in 60% yield, whereas **16** forms two isomeric ethers **18** and **19** in a ratio of 1:1 in 66% yield. Ethers **17** and **18** can be isolated in pure form and characterized (Scheme 1).

Within the framework of an investigation on the antiaromaticity of 4*n* p-electron compounds, it is of basic interest to find out how large the destabilization caused by the p-electron delocalization is. That is, in our case, by how many kcal/mol is carbocation **16**, in which the double bond (C6−C7) interacts homoconjugatively with the allyl cation fragment (C2−C3−C4), less stable than allyl cation **15**? The relative stabilities of carbocations **14−16** can be determined experimentally by means of ^{19}F NMR spectroscopy. Taft and McKeever found a correlation of 0.75 kcal/ppm for the electrochemically determined stabilities and the ^{19}F chemical shifts of 4-fluoro-4′-X- and 4-fluoro- 4′-X-4′′-X-trityl cations.[14] To determine the relative stabilities of carbocations **14**, **15**, and **16**, their ^{19}F chemical shifts were measured relative to the reference CCl_3F, and the differences of their shifts were multiplied by 0.75. From these results, **15** is 11.17 kcal/mol more stable than **14** and 3.7 kcal/mol more stable than **16**.

The twist angle (C3−C2−C1′−C2′) of the fluorophenyl substituent against the plane of the allyl cation segment (C2−C3−C4) was calculated to be $\theta = 13.3°$ in cation **15** and $\theta = 13.9°$ in cation **16**. This means that the observed relative stabilities of these cations are exclusively caused by their electron configurations.

An indication of a paramagnetic ring current and the homoantiaromatic character of carbocation **16** gave the low field shift of the proton signals of the $C(8)H_2$ group and the ^{13}C signal of C8 in **16** in comparison with that in **11−15**. The low-field shifts were found to be 0.9 to 1.0 ppm for the ^{1}H measurements and 20−26 ppm for the ^{13}C measurements (Tables S3 and S4, Supporting Information). In addition to the previous experimental studies, we have also executed DFT calculations (Table S1, Supporting Information) of compounds **11−18**.[11] All optimized structures (level: B3LYP/6-31G(d)) are characterized by harmonic frequence calculations. (All frequencies are real.)

The experimentally determined ^{1}H and ^{13}C chemical shifts of alcohols **11−13** and carbocations **14−16** as well as the ^{1}H chemical shifts of trapped ethers **17** and **18** (Tables S3 and S4, Supporting Information) agree well with the shifts calculated by the GIAO method on level B3LYP/6-311+G(2d,p)// B3LYP/6-31 G(d).

The relative stabilities of cations **14−16**, determined experimentally on the basis of the ^{19}F chemical shifts, agree relatively well with the relative stabilities determined by DFT calculations on level B3LYP/6-31G(d), under consideration of the zero-point correction and isodesmic reactions 1 and 2 (Scheme 2). According to the DFT calculations, **15** is more stable than **14** by 9.00 kcal/mol, and cation **16** is less stable than cation **15** by 3.18 kcal/mol, because of the homoconjugative interaction of the allyl cation fragment (C2−C3−C4) with the double bond (C6−C7) in carbocation **16**.[15]

A combination of geometric, energetic, and magnetic criteria well characterize the aromaticity or antiaromaticity of ring systems. The nucleus-independent chemical shift (NICS), the computation of the absolute magnetic shieldings at ring centers, is a widely used criterion of aromaticity.[16] Negative NICSs denote aromaticity, whereas positive NICSs denote antiaromaticity. Cation **16** has a NICS of +3.3 ppm that indicates that **16** is antiaromatic. This is in good agreement with its destabilization relative to cation **15** and the low-field shift of the proton signals of the $C(8)H_2$ group and the ^{13}C signal of C8 in **16** in comparison with that in **11−15**.

On the basis of the good agreement of the experimental and theoretical data of substituted carbocations **14−16**, we have determined the properties of unsubstituted carbocations **6**, **7**, **23**, **26**, **28**, and **30** by means of DFT calculations (structure and energy: level B3LYP/6-31G(d), NMR: level B3LYP/6-311+G-(2d,p)//B3LYP/6-31G(d), method GIAO).

In accordance with DFT calculations on level B3LYP/6-31G-(d), cation **7** is 6.07 kcal/mol more stable than homoantiaromatic carbocation **6**. The calculation of **6** on level B3LYP/6-311+G-(2d,p)//B3LYP/6-311+G(2d,p) yields no great change in its geometry, and under these conditions **7** is 6.66 kcal/mol more stable than **6**. The spatial neighborhood of sp^2-hybridized atoms C6 and C7 to allyl cation segment C2−C3−C4 in carbocation **6** is not the reason for its destabilization, as the comparison of carbocation **26** with cation **7** demonstrates in isodesmic eq 4. Cation **26** is 1.69 kcal/mol more stable than **7** and 8.12 kcal/mol more stable than **6** (Scheme 2). The NICS value of **6** is +4.17 ppm, which means that **6** is an antiaromatic ring system.

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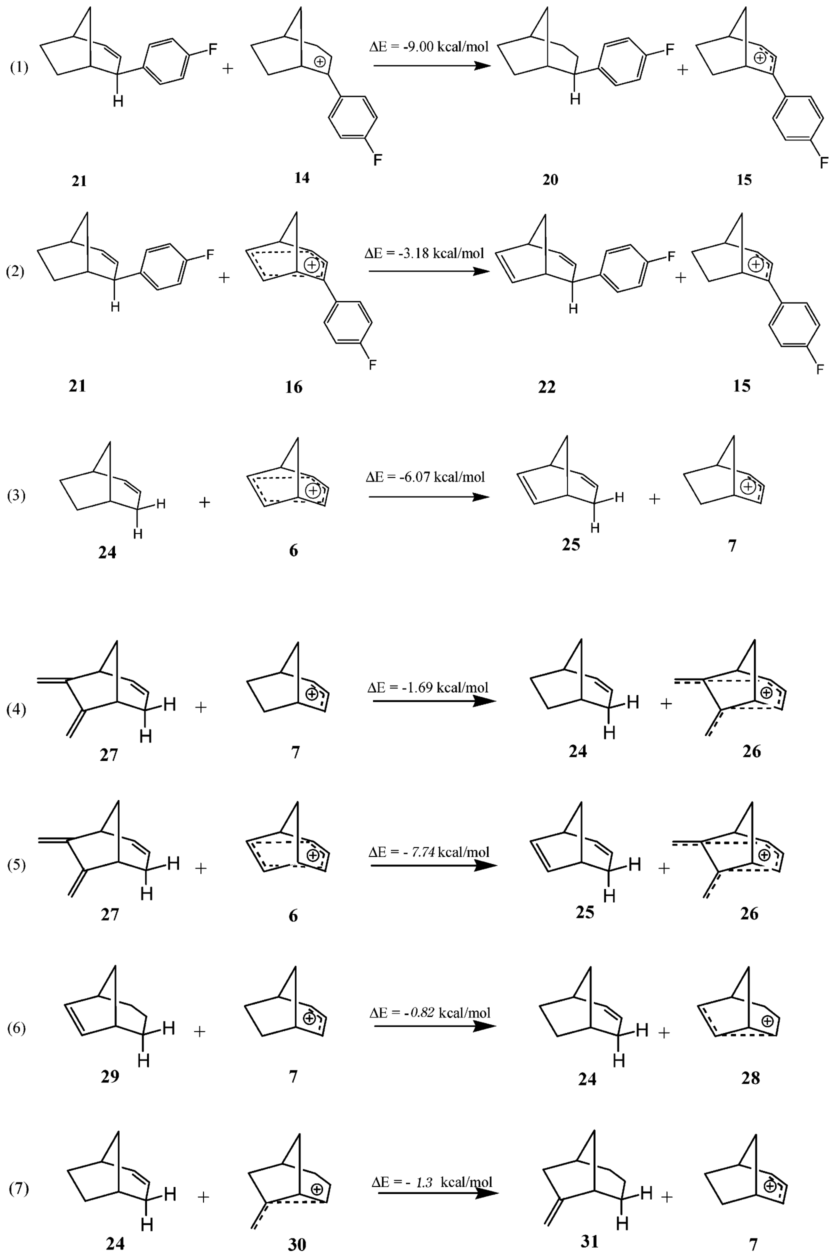
SCHEME 2. Relative Stabilities of Carbocations 6, 7, 14−16, 26, 28, and 30 As Determined by Isodesmic Reactions (Level B3LYP/6-31G(d)/(ZPC))

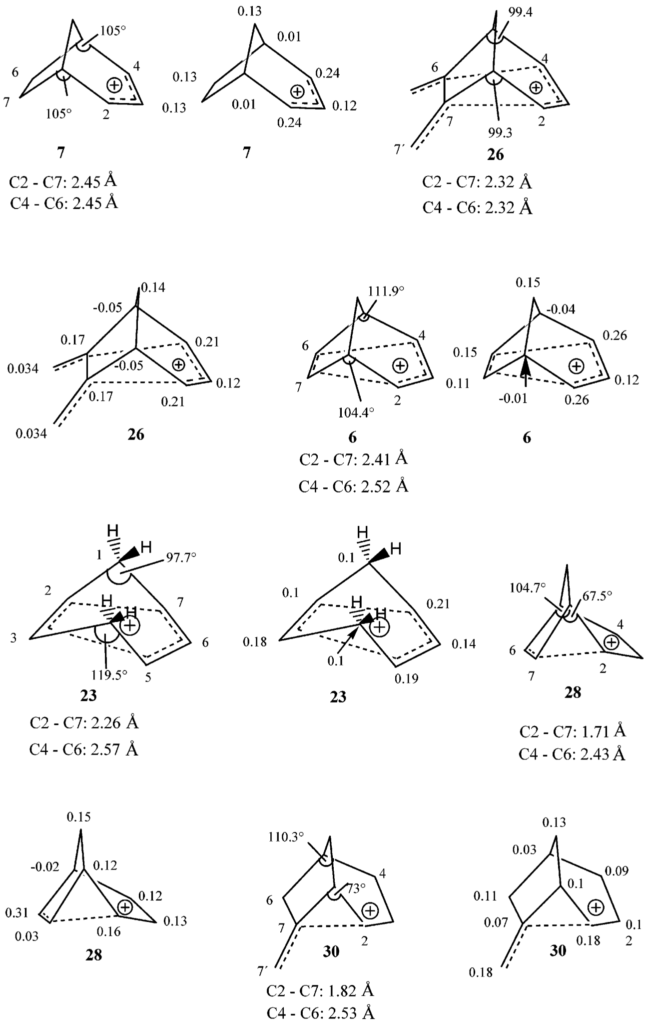


Whereas ab initio calculations of carbocation **6** on levels RHF/6-31G(d) and RMP2(fu)/6-31G(d)[10] yield the distances for C2−C7 and C4−C6 as well as for corresponding angles C2−C1−C7 and C4−C5−C6, the DFT calculation for **6** on level B3LYP/6-31G(d) yields a geometric distortion of the molecular structure. Distances C2−C7 and C4−C6 and corresponding angles C2−C1−C7 and C4−C5−C6 are no longer equally large (Scheme 3). That means that the destabilizing bishomoantiaromatic interaction in **6** is reduced to some extent by distortion. Consequently, the charge delocalization from the allyl fragment to the double bond (C6−C7) turns out to be no longer as uniform as in the two previously mentioned ab initio calculations. The deviation from the regular structure and charge distribution is even stronger in cation **23**, in which the clamp effect of C8 is missing (Scheme 3). However, distances C2−C7 and C4−C6 are the same, and the charge delocalization from the allyl anion segment to double bond C6−C7 is uniform in bishomoaromatic anion **8** (NICS = −7.62 ppm). (For NICS values, see also Table S7, Supporting Information.)

Besause of stabilizing homoconjugation in **26** distance C2−C7 is around 0.2 Å and distance C4−C6 is around 0.09 Å smaller than in **6,** and the charge densities are reduced in positions 2 and 4 in **26** to $q = 0.21$ because of charge delocalization (Scheme 3).

Because of homoconjugative interactions, the geometries of carbocations **28** and **30** are also relatively strongly changed in comparison with the regularly built bicyclo[3.2.1]octyl compounds. Whereas distances C2−C7 and C4−C6 are 2.45 Å each in **7** and 2.32 Å each in **26**, distance C2−C7 has shrunk in carbocation **28** to 1.71 Å. Its overlap population ρ (2−7) is 0.280, and the positive charge is delocalized mostly to the C6 atom (Scheme 3). Cation **28** is practically of the same stability as **7** (Scheme 2). Cation **30** is less stable than **7** by only 1.3 kcal/mol (Scheme 2). Distance C2−C7 in **30** is 1.82 Å, with a

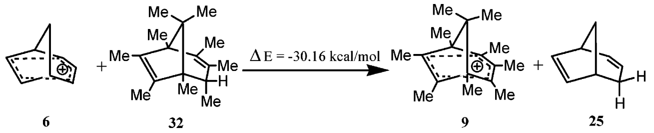
SCHEME 3. Optimized Geometries and Charge Densities of Carbocations 6, 7, 23, 26, 28, and 30 As Determined by DFT Calculations (B3LYP/6-31G(d))



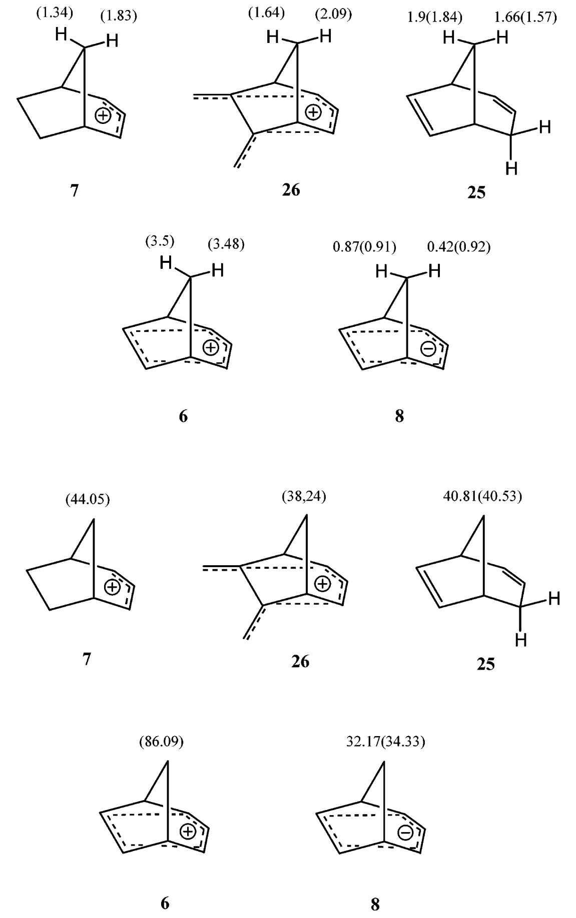
corresponding overlap population ρ (2−7) = 0.165, and the charges on C2 and C7′ are practically the same (Scheme 3).

The comparison of the calculated ^{1}H chemical shifts (level B3LYP/6-311+G (2d, p)//B3LYP/6-31G(d)) of the protons at bridge atom C8 of cation **6** and anion **8** with those of cations **7** and **26** and hydrocarbon **25** shows a low-field shift in the case of **6**, which supports the existence of a paramagnetic ring current and the bishomoantiaromatic character of **6**. In comparison with hydrocarbon **25**, high field shifts are observed for anion **8** in experiments[17] and calculations. This indicates a diamagnetic ring current and therefore bishomoaromatic character for **8**. One arrives at the same conclusion if one looks at the ^{13}C chemical shifts of C8 in the respective group of compounds (Scheme 4).

Finally, it should be mentioned that because of DFT calculations the nine methyl substituents in nonamethylbicyclo[3.2.1]-octa-3,6-dien-2-yl cation **9** cause a stabilization of 30 kcal/mol relative to unsubstituted bicyclo[3.2.1]octa-3,6-dien-2-yl cation **6**.



SCHEME 4. Chemical Shifts of Bridge Carbon C8 and the Corresponding Bridge Hydrogens (C8)H_2[a]



[a] Calculated chemical shifts are in parentheses.

Conclusions

Carbocations **14**−**16** were prepared from carbinols **11**−**13** and were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy and quenching experiments of **15** and **16**. Cation **16** is experimentally less stable than **15** by 3.7 kcal/mol, and the bridge protons on C8 in **16** are shifted to a lower field. DFT calculations yield the same tendency of destabilization for **16**. Its NICS value is +3.3 ppm, which means, in summary, that **16** is a bishomoantiaromatic system. In general, the calculated ^{1}H and ^{13}C chemical shifts of alcohols **11**−**13**, carbocations **14**−**16**, and ethers **17** and **18** as well as the calculated relative stabilities of cations **15** and **16** are in good agreement with the experimental values. Furthermore, we have executed DFT calculations of unsubstituted carbocations **6**, **7**, **26**, **28**, and **30**. The comparison of **6** with **26** shows that the inductive effect of sp^{2}-hybridized atoms C6 and C7 is not responsible for the destabilization of **6**. The results for **6** indicate that it is less stable than **7** by 6.07 kcal/mol, and its NICS value is +4.17 ppm, which means that **6** is a bishomoantiaromtic cation. This is in good agreement with the calculated exaltation of magnetic susceptibility by Jiao and Schleyer.[10] The homoconjugation in carbocation **28** is as effective as the allyl conjugation in **7**. The NICS value for anion **8** of −7.62 ppm documents its bishomoaromatic character.

It can generally be noted that the bicyclo[3.2.1]octyl cations and anions are good model compounds for the study of homoconjugation.

Experimental Section

The ketones bicyclo[3.2.1]octa-3,6-dien-2-one and bicyclo[3.2.1]-octa-3-en-2-one were prepared by known literature methods.[19,20]

General Procedure for the Preparation of Carbinols as Exemplified by the Preparation of 2-(4′-Fluorophenyl)bicyclo-[3.2.1]octa-3,6-dien-2-ol 13. Magnesium slivers (0.05 mol) were suspended in abs ether (10 mL), and to this suspension was added under stirring 1-bromo-4-fluorobenzene (0.038 mol) dissolved in abs ether (20 mL). This mixture was then heated for 3 h at reflux. Thereupon, a solution of bicyclo[3.2.1]octa-3,6-dien-2-one (0.025 mol) in abs ether (20 mL) was added to the Grignard solution under stirring. After the addition of the ketone solution, the mixture was heated for another 2 h under stirring at reflux. After this, the reaction mixture was cooled and hydrolyzed by means of ice (30 g), and the precipitate was dissolved by the addition of sat. NH_4Cl solution. The ether phase was separated, and the aqueous phase was extracted three times with 100 mL of ether each. The united ether solutions were washed with a little water and thereupon dried over Na_2SO_4. After removing the ether, we purified the raw carbinol yield by MPLC (SiO_2/CH_2Cl_2; $d = 20$ mm/h = 450 mm).

2-(4′-Fluorophenyl)bicyclo[3.2.1]octa-3,6-dien-2-ol 13. Oil. IR (film) ν (cm^{-1}): 3560, 3420, 3050, 2940, 2860, 1600, 1500, 1220, 1160, 1040, 1010, 920, 830, 740. ^{1}H NMR ($CDCl_3$, TMS): δ 7.55 (dd, $J = 8.6$, 5.7 Hz, 2H; $H2'_{ar}$, $H6'_{ar}$), 7.00 (t, $J = 8.6$ Hz, 2H; $H3'_{ar}$, $H5'_{ar}$), 6.64 (dd, $J = 5.5$, 3.0 Hz, 1H; H6), 6.48 (dd, $J = 9.5$, 6.0 Hz, 1H; H4), 6.01 (dd, $J = 5.5$, 3.0 Hz, 1H; H7), 5.27 (dd, $J = 9.5$, 2.2 Hz, 1H; H3), 3.03 (m, 1H; H1), 2.68 (m, 1H; H5), 1.94 (t, $J = 2.5$ Hz, 2H; H8a, H8b). ^{13}C NMR ($CDCl_3$, TMS): δ 162.0 (d, $J = 242$ Hz, 1C; $C4'_{ar}$), 145.7 (1C; C6), 143.3 (d, $J = 2.7$ Hz, 1C; $C1'_{ar}$), 137.3 (1C; C4), 131.8 (1C; C7), 129.0 (1C; C3), 128.1 (d, $J = 8.7$ Hz, 2C; $C2'_{ar}$, $C6'_{ar}$), 114.7 (d, $J = 20.5$ Hz, 2C; $C3'_{ar}$, $C5'_{ar}$), 74.1 (1C; C2), 59.8 (1C; C1), 43.3 (1C; C8), 39.26 (1C; C5). ^{19}F NMR ($CDCl_3$, CCl_3F): δ −115.14. MS (70 eV, EI) *m/z*: 216 [M]$^+$. Anal. Calcd for $C_{14}H_{13}FO$ (216.25): C, 77.76; H, 6.06. Found: C, 77.45; H, 6.03.

2-(4′-Fluorophenyl)bicyclo[3.2.1]oct-3-en-2-ol 12. Oil. IR (film) ν (cm^{-1}): 3600, 3420, 3010, 2950, 2870, 1600, 1500, 1450, 1300, 1220, 1150, 1080, 1050, 980, 940, 880, 830, 820, 750. ^{1}H NMR ($CDCl_3$, TMS): δ 7.34 (dd, $J = 8.6$, 5.7 Hz, 2H; $H2'_{ar}$, $H6'_{ar}$), 7.01 (t, $J = 8.6$ Hz, 2H; $H3'_{ar}$, $H5'_{ar}$), 6.16 (dd, $J = 10.0$, 6.4 Hz, 1H; H4), 5.37 (dd, $J = 10.0$, 3.0 Hz 1H; H3), 2.4 (m, 2H; H1, H5), 1.88 (m, 2H; $H6_{exo}$, $H7_{exo}$), 1.7 (m, 2H; H8a, H8b), 1.33 (m, 2H; $H6_{endo}$, $H7_{endo}$). ^{13}C NMR ($CDCl_3$, TMS): δ 161.9 (d, $J = 246$ Hz, 1C; $C4'_{ar}$), 143.2 (d, $J = 4.3$ Hz, 1C; $C1'_{ar}$), 136.2 (1C; C4), 128.3 (1C; C3), 128.2 (d, $J = 7.3$ Hz, 2C; $C2'_{ar}$, $C6'_{ar}$), 114.5 (d, $J = 20$ Hz, 2C; $C3'_{ar}$, $C5'_{ar}$), 78.7 (1C; C2), 47.8 (1C; C1), 35.6 (1C; C5), 35.5 (1C; C8), 31.6 (1C; C6), 22.8 (1C; C7). ^{19}F NMR ($CDCl_3$, CCl_3F): δ −115.69. MS (70 eV, EI) *m/z*: 218 [M]$^+$. Anal. Calcd for $C_{14}H_{15}FO$ (218.27): C, 77.04; H, 6.93. Found: C, 76.83; H, 7.00.

2-(4′-Fluorophenyl)bicyclo[3.2.1]octan-2-ol 11. The title compound was synthesized by catalytic hydrogenation (Pd/C−H_2; ethanol; rt) of **13**. Oil. IR (film) ν (cm^{-1}): 2940, 2870, 2820, 1600, 1500, 1450, 1220, 1160, 1080, 1050, 1010, 830. ^{1}H NMR ($CDCl_3$, TMS): δ 7.51 (dd, $J = 8.6$, 5.7 Hz, 2H; $H2'_{ar}$, $H6'_{ar}$), 7.04 (t, $J = 8.6$ Hz, 2H; $H3'_{ar}$, $H5'_{ar}$), 2.46 (m, 1H; H1), 2.15 (m, 1H; H5), 1.60 (m, 2H; H8a, H8b), 1.45 (m, 8H; $H3_{exo}$, $H3_{endo}$, $H4_{exo}$, $H4_{endo}$, $H6_{exo}$, $H6_{endo}$, $H7_{exo}$, $H7_{endo}$). ^{13}C NMR ($CDCl_3$, TMS): δ 161.7 (d, $J = 244.6$ Hz, 1C; $C4'_{ar}$), 142.4 (d, $J = 2.9$ Hz, 1C; $C1'_{ar}$), 127.9 (d, $J = 8.78$ Hz, 2C; $C2'_{ar}$, $C6'_{ar}$), 114.8 (d, $J = 20.5$ Hz, 2C; $C3'_{ar}$, $C5'_{ar}$), 75.4 (1C; C2), 47.3 (1C; C1), 35.3 (1C; C3), 34.2 (1C; C5), 31.7 (1C; C4), 28.9 (2C; C6, C8), 25.2 (1C; C7).^{19}F NMR ($CDCl_3$, CCl_3F): δ −115.35. MS (70 eV, EI) *m/z*: 220 [M]$^+$. Anal. Calcd for $C_{14}H_{17}FO$ (220.28): C, 76.33; H, 7.78. Found: C, 76.15; H, 7.75.

Preparation of Carbocations 14−16. The reactions were executed in cation equipment under a protective nitrogen atmosphere (Scheme S1, Supporting Information). The carbinols (0.115 mmol) were dissolved in CD_2Cl_2 (0.2 mL) and added under vigorous stirring as droplets to a mixture of fluorosulfuric acid (0.1 mL, 1.743 × 10^{-3} mol) and sulfuryl chloride fluoride (50 drops) cooled to −120 °C. The mixture was stirred for an additional 15 min and then transferred to an NMR tube.

2-(4′-Fluorophenyl)bicyclo[3.2.1]octan-2-yl Cation 14. ^{1}H NMR ($FSO_3H//SO_2ClF/CD_2Cl_2$, −50 °C, $CHDCl_2$): δ 8.95 (dd, $J = 8.6$, 5.7 Hz, 2H; $H2'_{ar}$, $H6'_{ar}$), 7.7 (t, $J = 8.6$ Hz, 2H; $H3'_{ar}$, $H5'_{ar}$), 4.65 (m, 1H; H1), 4.02 (m, 1H; $H3_{endo}$), 3.5 (m, 1H; $H3_{exo}$), 2.17 (m, 2H; H8a, H8b), 2.37 (m, 7H; $H4_{exo}$, $H4_{endo}$, H5, $H6_{exo}$, $H6_{endo}$, $H7_{exo}$, $H7_{endo}$). ^{13}C NMR ($FSO_3H/SO_2ClF/CD_2Cl_2$, −50 °C, $CHDCl_2$): δ 256.9 (1C; C2), 179.3 (d, $J = 290.04$ Hz, 1C; $C4'_{ar}$), 144.8 (d, $J = 16.1$ Hz, 1C; $C6'_{ar}$), 143.8 (d, $J = 16.1$ Hz, 1C; $C2'_{ar}$), 133.5 (1C; $C1'_{ar}$), 121.3 (d, $J = 23.4$ Hz, 2C; $C3'_{ar}$, $C5'_{ar}$), 52.9 (1C; C1), 48.1 (1C; C3), 43.7 (1C; C5), 37.3 (1C; C7), 36.7 (1C; C8), 34.5 (1C; C6), 28.8 (1C; C4). ^{19}F NMR ($FSO_3H/SO_2ClF/CDCl_3$, −50 °C, CCl_3F-ex): δ −65.67.

2-(4′-Fluorophenyl)bicyclo[3.2.1]oct-3-en-2-yl Cation 15. ^{1}H NMR ($FSO_3H//SO_2ClF/CD_2Cl_2$, −50 °C, $CHDCl_2$): δ 9.14 (t, $J = 8.0$ Hz, 1H; H4), 8.67 (dd, $J = 8.6$, 5.7 Hz, 2H; $H2'_{ar}$, $H6'_{ar}$), 8.02 (dd, $J = 8.0$, 1.6 Hz, 1H; H3), 7.64 ((t, $J = 8.6$ Hz, 2H; $H3'_{ar}$, $H5'_{ar}$), 4.6 (dd, $J = 7.0$, 4.0 Hz, 1H; H1), 3.9 (sex, $J = 10.3$ Hz, 1H; H5), 2.9 ((m, 2H; $H6_{exo}$, $H7_{exo}$), 2.06 (d, $J_{gem} = 11.0$ Hz, 1H; H8b), 1.86 (d, $J_{gem} = 11.0$ Hz, 1H; H8a), 1.8 (m, 1H; $H6_{endo}$), 1.5 (m, 1H; $H7_{endo}$). ^{13}C NMR ($FSO_3H/SO_2ClF/CD_2Cl_2$, −50 °C, $CHDCl_2$): δ 210.4 (1C; C2), 193.4 (1C; C4), 174.1 (d, $J = 278.32$ Hz, 1C; $C4'_{ar}$), 140.9 (d, $J = 16.1$ Hz, 2C; $C2'_{ar}$, $C6'_{ar}$), 129.9 (1C; $C1'_{ar}$), 120.5 (1C; C3), 119.9 (d, $J = 23.4$ Hz, 2C; $C3'_{ar}$, $C5'_{ar}$), 47.3 (1C; C1), 45.2 (1C; C5), 43.1 (1C; C8), 27.8 (1C; C6), 26.9 (1C; C7). ^{19}F NMR ($FSO_3H/SO_2ClF/CDCl_3$, −50 °C, CCl_3F-ex): δ −80.56.

2-(4′-Fluorophenyl)bicyclo[3.2.1]oct-3,6-dien-2-yl Cation 16. ^{1}H NMR ($FSO_3H//SO_2ClF/CD_2Cl_2$, −50 °C, $CHDCl_2$): δ 9.35 (dd, $J = 9.2$, 7.0 Hz, 1H; H4), 8.73 (m, 2H; $H2'_{ar}$, $H6'_{ar}$), 7.65 (t, $J = 8.0$ Hz, 2H; $H3'_{ar}$, $H5'_{ar}$), 7.64 (t, $J = 9.0$ Hz, 1H; H3), 7.27 (t, $J = 4.0$ Hz, 1H; H6), 6.84 (t, $J = 4.0$ Hz, 1H; H7), 4.9 (br s, 1 H; H1), 4.13 (quin, $J = 9.2$, 7.0 Hz, 1H; H5), 3.05 (m, 2H; H8a, H8b). ^{13}C NMR ($FSO_3H//SO_2ClF/CD_2Cl_2$, −50 °C, $CHDCl_2$): δ 209.0 (1C; C2), 192.4 (1C; C4), 175.6 (d, $J = 282.71$ Hz, 1C; $C4'_{ar}$), 146.0 (1C; C6), 142.3 (d, $J = 14.6$ Hz, 1C; $C6'_{ar}$), 140.3 (d, $J = 14.6$ Hz, 1C; $C2'_{ar}$), 135.3 (1C; C7), 132.1 (1C; $C1'_{ar}$), 128.1 (1C; C3), 120.5 (d, $J = 21.9$ Hz, 1C; $C5'_{ar}$), 120.3 (d, $J = 21.9$ Hz, 1C; $C3'_{ar}$), 63.1 (1C; C8), 53.3 (1C; C1), 50.5 (1C; C5). ^{19}F NMR ($FSO_3H/SO_2ClF/CDCl_3$, −50 °C, CCl_3F-ex): δ −75.63.

Quenching of Carbocations with $NaOCH_3/HOCH_3$. The carbocation solution was cooled to −120 °C and sprayed by passing it through a capillary to produce micro drops that were quenched by a −120 °C solution of Na (2.5 g) in CH_3OH (80 mL). The resulting crude product was worked up by preparative thin-layer chromatography.

2-(4′-Fluorophenyl)-4-methoxybicyclo[3.2.1]oct-2-ene 17. Oil. 158 mg (68% yield). IR (film) ν (cm^{-1}): 3030, 2950, 2878, 2810, 1600, 1510, 1450, 1370, 1230, 1190, 1150, 1090, 1080, 970, 940, 820. ^{1}H NMR ($CDCl_3$, TMS): δ 7.4 (dd, $J = 8.6$, 5.7 Hz, 2H; $H2'_{ar}$, $H6'_{ar}$), 7.0 (t, $J = 8.6$ Hz, 2H; $H3'_{ar}$, $H5'_{ar}$), 5.77 (d, $J = 5.0$ Hz, 1H; H3), 3.42 (s, 3H; OCH3; d, $J = 5.0$ Hz, 1H; H4), 2.93 (m, 1H; H1), 2.58 (m, 1H; H5), 1.8 (m, 4H; $H6_{endo}$, $H7_{endo}$, H8a, H8b), 1.33 (m, 2H; $H6_{exo}$, $H7_{exo}$). MS (70 eV, EI) *m/z*: 232 [M]$^+$. Anal. Calcd for $C_{15}H_{17}OF$ (232.29): C, 77.56; H, 7.38. Found: C, 77.23; H 6.95.

2-(4′-Fluorophenyl)-4-methoxybicyclo[3.2.1]octa-2,6-diene 18. Oil (isomer, OCH_{3endo}); 61.9 mg (19.4% yield). IR (film) ν (cm^{-1}): 3060, 2940, 2810, 1600, 1500, 1450, 1340, 1225, 1160, 1090, 970, 825, 740, 700. ^{1}H NMR ($CDCl_3$, TMS): δ 7.35 (dd, $J = 8.6$, 5.7 Hz, 2H; $H2'_{ar}$, $H6'_{ar}$), 7.0 (t, $J = 8.6$ Hz, 2H; $H3'_{ar}$, $H5'_{ar}$), 6.6 (dd, $J = 5.5$, 3.0 Hz, 1H; H7), 5.93 (dd, $J = 5.5$, 3.0 Hz, 1H; H6), 5.5 (m, 1H; H3), 4.08 (m, 1H; H4), 3.44 (s, 3H; OCH3), 3.24 (m, 1H; H5), 2.91 (m, 1H; H1), 2.24 (m, 1H; H8a), 2.04 (m, 1H; H8b). MS (70 ev, EI, $C_{15}H_{15}FO$, M = 230.38) *m/z*: 230 [M]$^+$.

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Supporting Information Available: General experimental details, calculated energies and geometries for compounds in this article, experimental and calculated ^{1}H, ^{13}C, and ^{19}F chemical shifts, and NICS values calculated at different levels. This material is available free of charge via the Internet at http://pubs.acs.org.

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